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by

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Degradation of Poly(methylphenylsilylene) and Poly(di-n-hexylsilylene)

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Abstract

Degradation of poly(methylphenylsilylene) and poly(di-n-hexylsilylene) was studied by chemical and mechanical methods at ambient and higher temperatures. Purely thermal degradation in solid state starts as a slow process at 150 ^0C and provides soluble and insoluble products which include cyclosilanes as well as various siloxanes. Sonication at ambient temperatures leads to the mechanical degradation of high molecular weight polymers by homolytic cleavage induced by shear forces. No cyclics are formed under these conditions. Polysilanes in the presence of strong nucleophiles degrade exclusively to cyclic oligomers. Rate of this backbiting chain reaction depends on substituents at silicon atom, alkali metal, solvents, and temperature. Electrophiles degrade polysilanes to various α, ω-difunctional oligosilanes.

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Introduction

Photochemical degradation of polysilylenes (polysilanes) is well known and understood[1,2]. It proceeds via various intermediates such as silyl radicals and silylenes, depending on the energy of the irradiation. Photobleaching is observed upon photodegradation, because UV absorption is molecular weight dependent. These properties make polysilanes applicable as positive photoresists suitable for dry development, and also as imageable etch barriers and contrast enhancement layers[1,2]. On the other hand, much less is known about the chemical and mechanical stability of polysilanes. Polysilanes are usually prepared by the reductive coupling of disubstituted dichlorosilanes with alkali metals[3,4,5]. This process is accompanied by the formation of a large amount of cyclopolysilanes. Reductive coupling conditions which are "too harsh" may lead to the complete degradation of polysilanes to low molecular weight cyclopolysilanes[6,7]. Thus, linear high molecular weight polysilane is a kinetic rather than a thermodynamic product. Si-Si bonds in low molecular weight silanes can be cleaved by various nucleophiles and electrophiles; in a similar way polysilane can be degraded. Ultrasound generates cavities which can degrade polymers by mechanical forces during sonication process. In this way chain rupture can occur not only in organic polymers but also in polysilanes. In this paper thermal, sonochemical and chemical degradation of poly(methylphenylsilylene) and poly(di-n-hexylsilylene) is described.

Experimental

1. Thermal Degradation

A sample of poly(methylphenylsilylene) (ca. 7 mg) was placed in an aluminium pan and then was sealed with an aluminium cover using a sample pan crimper. An aluminium pan was heated in an oven and also in a DSC heater system at 150 ^oC, 240 ^oC and 280 ^oC in nitrogen atmosphere.

A sample of poly(methylphenylsilylene) was dissolved in decalin and heated at 150 ^oC and 190 ^oC under dry nitrogen. The products at various degradation times were analyzed by GPC , UV, IR, ^1H and ^{29}Si NMR.

2. Sonochemical Degradation

A test tube fit with a rubber septum was thoroughly dried with a flame and purged with dried argon gas. It was placed in an ultrasonic cleaner (75-1970 Ultramet II Sonic Cleaner, Buehler Ltd.) or fitted with an immersion-type probe (W-385, Heat Systems-Ultrasonic, Inc.). A precise amount of alkali metal (10% wt. of polysilane) and 10 ml toluene were added to the dried test tube. The mixture was irradiated by ultrasound until a high quality of sodium dispersion is formed. A toluene solution of polysilane at various concentrations was added to the sodium dispersion using a syringe. The polysilane solution was irradiated by ultrasound. In some experiments, toluene solutions of polysilanes were irradiated by ultrasound without Na. The degraded polymers, at various irradiation times, were analyzed by ^1H NMR, UV, and GPC.

3. Chemical Degradation

(a) by Alkali Metals

A flask was sealed with a septum and thoroughly dried with a flame under inert argon. Precise amounts of alkali metals or homogeneous chemical reductants in THF (Na or Li/ naphthalenide) were added to the flask under argon gas. THF solutions (0.8% wt.) of polysilanes were added to the flask using a syringe. The mixtures were stirred at room temperature in the dark. The final polymers were analyzed by GPC at various times. Molecular weights and polydispersities were determined by GPC using polystyrene standards. The degraded polysilanes were analyzed by GPC, ^{1}H NMR, and ^{29}Si NMR.

(b) by Iodine

Known amounts of polysilanes and iodine (I_2) were dissolved in CH_2Cl_2 in 10 ml flasks. The iodine solution was added dropwise to the stirred polysilane solution using a syringe. The solution was kept in the dark overnight. The completion of the reaction was checked by UV with the disappearance of the absorption of I_2 at 504 nm. The Si-I bonds are unstable to the moisture. Therefore, molecular weights and polydispersities were determined by GPC after reaction with PhMgBr. The degraded polysilanes were analyzed by GPC and ^{1}H NMR.

4. Materials and Equipment

Poly(methylphenylsilylene) and poly(di-n-hexylsilylene) were prepared according to previously published procedures using either

sonochemical or thermal reductive coupling of the dichlorosilanes with sodium[5,6,7].

GPC analysis was carried out in THF solutions using Waters GPC with Ultrastyragel columns, 510 pump, 410 refractive index detector and 450 UV detector. ^{1}H and ^{29}Si NMR spectra were recorded with a IBM 300 MHz NR-300 instrument. UV spectra were recorded with IBM 9430 UV-Vis spectrometer or Hewlett Packard 8452 UV-diode array spectrometer. IR spectra were measured with a Nicolet 5-DX FTIR instrument.

Results and Discussion

Thermal Decomposition

Thermal degradation of poly(methylphenylsilylene) has been carried out at various temperatures in the solid state and in solution. The results of the thermal decomposition of poly(methylphenyl-silylene) in the solid state are summarized in Fig. 1. GPC traces show that thermal degradation led to a decrease in the molecular weight and the formation of cyclics. Decomposition of poly(methyl-phenylsilylene) in the solid state starts at approximately 150 °C and is accompanied by the formation of a fraction soluble and insoluble (10-25 %) in organic solvents (THF or toluene).

The soluble fraction consisted of a mixture of a polymer and cycles. The molecular weight of the polymer decreased with degradation time. After 24 hours at 150 °C, nearly half of the polymer was converted to cycles. The molecular weight of a soluble polymer was reduced from M_n= 85,000 to M_n= 2,900. Polydispersity

increased from 1.63 to 3.22. A similar decrease in the molecular weight requires 3 hours at 240 °C and 0.5 hour at 280 °C. The rate of thermal degradation increases with the degradation temperature. After 2 hours at 240 °C, 30 % of an insoluble polymer was formed. The soluble degraded polymer (M_n= 2,900) absorbed at 323 nm (Fig. 2). This wavelength is by 15 nm lower than that of a polymer before degradation. Absorption maximum of poly(methylphenylsilylene) depends on the length of the non-interrupted Si-Si bonds (molecular weight). However, polymers of a similar molecular weight prepared under different conditions absorbed at 338 nm. This might indicate incorporation of oxygen into polysilane chains, formation of Si-O-Si linkages and decrease of Si-Si conjugation length. Cyclics and polysilane degraded in the presence of air, contain Si-O-Si bonds, as observed at 1100 cm^{-1} by IR spectroscopy (Fig. 3)

Fig. 4 shows the change of M_n for a solution of poly(methyl-phenylsilylene) during thermal degradation in decalin at 150 °C and at 190 °C. At 150 °C, degradation occurred very slowly; after 23 hours, 10 % of the polymer was converted into cyclics and the molecular weight was decreased two times. After 4.5 hours at 190 °C, 5 % of the polymer was converted into cyclics. The molecular weight decreased from 136,000 to 59,000, but polydispersity increased from 1.49 to 2.03. Thermal degradation was slower in solution than in the solid state. After 22 hours at 190 °C, degradation led to the formation of cyclics (60 %) and a soluble polymer with M_n= 2,000 and very high polydispersity. No insoluble polymer was formed by degradation in solution.

Thermal degradation reported here has been studied in a time scale much longer than use typically in thermogravimetric analysis (10 K/min). Thus, degradation was observed at lower temperatures than previously reported ($\approx$300 °C [3] or 226 °C [8] as found for poly(di-n-hexylsilylene)).

A possible thermal degradation mechanism[9] is shown in Scheme 1. Si-Si bonds are homolytically cleaved to form radical species. Some radical species might react with aromatic groups in poly(methylphenylsilylene) in the solid state to yield a crosslinked, insoluble polymer. In solution, radical species could rather react with a solvent and keep degrading polymer in solution. Radical species could participate in backbiting process which directly generates cyclics. Cyclics might be also formed by silylene intermediates.

A typical reductive coupling process is run at temperatures not exceeding 100 °C, and therefore thermal decomposition can be neglected during the synthesis.

Sonochemical Degradation

Sonochemical polymerization in toluene at ambient temperatures leads to monomodal polysilanes with relatively high molecular weights ($M_n \approx$ 100,000). Formation of a low molecular weight fraction ($M_n \approx$ 5,000) is usually suppressed under these conditions[6,10,11] We have explained the monomodal molecular weight *distributions* by *elimination* of *reactions* responsible for the formation of the low molecular weight fraction. Apparently, they have higher activation energies than propagation. Decrease of molecular weights to the limiting value of $M_n \approx$ 50,000 has been

observed with prolonged sonication in toluene. Sonication led to decrease of polydispersities ($M_w/M_n < 1.5$, and even down to $M_w/M_n = 1.2$) [6]. Examples of the decrease of molecular weights and polydispersities are presented in Table 1 and Fig. 5. The decrease of molecular weight in both poly(methylphenylsilylene) and poly(di-n-hexylsilylene) can be attributed to homolytic cleavage of Si-Si bonds by shear forces induced by cavitation. The decrease of polydispersities could originate in the selective cleavage of the chains with a molecular weight sufficiently high to be involved in chain entanglement. Similar action of ultrasound has been previously described for other organic polymers[12]. Sonochemical degradation is based on frictional forces between the more mobile solvent molecules and the less mobile macromolecules during the cavitation process. This mechanism requires the presence of entanglement between degrading chains. Chains with lower molecular weight can not entangle efficiently or can relax during cavitation process before chain rupture. The effect of concentration of polysilane solutions on degradation is shown in Fig. 6. The rate of the sonochemical degradation increases with concentration, but is weakly affected at concentrations above 0.8 %. This is probably related to the intermolecular chain entanglement, which occurs above this concentration. In more dilute solution (0.2% wt.), chain entanglement limits polysilane degradation. Under this condition, sonochemical degradation occurs very slowly and the higher limiting molecular weights are observed.

Qualitatively similar results have been obtained in sonochemical degradations of polystyrene as well as other organic

polymers[12,13,14]. Si-Si bond is weaker (80 kcal/mol) than C-C bond and the chain rupture is easier for polysilanes than for organic polymers. Therefore degradation occurs at lower energies and provides lower molecular weight polymers.

Degradation of poly(methylphenylsilylene) in the presence of sodium dispersion proceeds slightly faster (Fig. 5). This may indicate either the generation of additional radical anions (or other "weak points") on the polysilane backbone or additional mechanical action of Na particles. Sonochemical degradation of poly(methylphenylsilylene) was also studied with Li and K. In the case of K, the rate of degradation is intermediate between with Na and without Na. The degradation rate with Li was similar to the rate without Na.

Cyclopolysilanes have not been detected during the sonochemical degradation in toluene in the presence of alkali metals, in contrast to chemical degradation discussed in the next section. Thus, the unusual molecular weight distribution observed in sonochemical synthesis originates from two phenomena: mechanical degradation of the very high molecular weight fraction and suppression of side reactions that lead to low polymer[10]. The low polymer does not entangle and can not be degraded by ultrasound. The lower limit for the sonochemical degradation is M_n= 50,000 at the frequency of 20 kHz.

The homolytic cleavage of Si-Si bonds leads to the formation of radicals as shown in Scheme 2. During degradation at ambient temperatures, in contrast to thermal degradation, no cyclics are observed. Therefore, at lower temperatures either silylenes are not
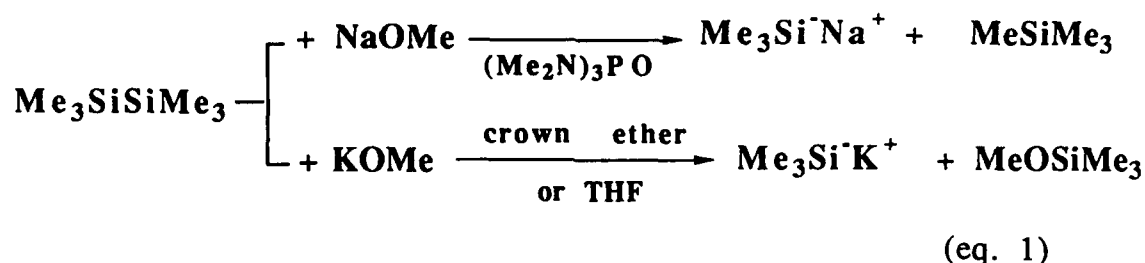
formed or radical depropagation by back biting is not effective The fate of the radicals is not known. Silyl radicals could react with toluene to produce a final product containing toluene end groups. The rate constant of the reaction of triethylsilyl radical with toluene is 10^6 $M^{-1}s^{-1}$ at ambient temperature[15]. In order to test the possibility of the reaction of toluene with silyl radicals, formed during sonochemical degradation, a high molecular weight poly(methylphenylsilylene) (M_n= 2.0 x 10^5) was used, in which Si-Si bonds could be cleaved four times to reach a reduced limited molecular weight ($M_n \approx$ 5 x10^4). The final product was analyzed by ^{1}H NMR. The ^{1}H NMR spectra of the methyl groups in poly(methylphenylsilylene) and in the degraded product are shown in Fig. 7. The ^{1}H NMR spectrum of the degraded product shows a very weak peak of methyl groups in the toluene moiety at 2.32 ppm. The integration area ratio of the methyl groups in the toluene moiety to that of methyl groups in poly(methylphenylsilylene) is 0.5%, which agrees with the predicted proportion of end-groups in the final product based on the molecular weight estimated from GPC.

Chemical Degradation of Polysilanes

A. Cleavage of Si-Si Bond by Nucleophiles

The action of strong nucleophiles on disilanes leads to the formation of silyl anions which are very reactive species. There are a few methods for generation of silyl anions. The first method is the reaction of disilanes with alkali metals[16]. The rate of this reaction increases with a number of aryl groups attached to silicon. Thus, the most efficient reaction is with hexaphenyldisilane ($Ph_3SiSiPh_3$), and

the least efficient is with hexamethyldisilane ($Me_3SiSiMe_3$). The reactions require nucleophilic solvents which can solvate alkali metal cations, such as THF, diglyme, HMPT, or ether. Trimethylsilyl anion ($Me_3Si^-Mt^+$) can be generated by sodium and potassium alkoxides in the presence of crown ethers [17]:

$$Me_3SiSiMe_3 \begin{cases} + \text{ NaOMe} \xrightarrow{(Me_2N)_3PO} Me_3Si^-Na^+ + MeSiMe_3 \\ + \text{ KOMe} \xrightarrow[\text{or THF}]{\text{crown ether}} Me_3Si^-K^+ + MeOSiMe_3 \end{cases}$$

(eq. 1)

Trialkylsilyl anions can also be formed from disilanes and methyl lithium [18]:

$$Me_3SiSiMe_3 + MeLi \xrightarrow{HMPT} Me_3Si^-Li^+ + Me_4Si$$

(eq. 2)

Polysilanes are usually prepared by the reductive coupling of disubstituted dichlorosilanes with alkali metals in nonpolar solvents[3,4,5], such as toluene or heptane[19]. No substantial degradation of the polymer is observed in the presence of an excess of alkali metal under these condition. In THF or diglyme, polysilanes can be degraded by an excess of alkali metal. The degradation products are essentially cyclic oligomers. The rate of degradation depends on the substituents on the silicon atom, on the solvent, on the alkali metal, and on temperature. Qualitative degradation results are shown in Table 2.

Chemical degradation of polysilanes with alkali metals is much faster in THF than in toluene due to the solvation of alkali metal

cations. For example, poly(methylphenylsilylene) was degraded with K in THF within 10 minutes, but degradation of polysilanes with alkali metals in toluene does not occur. Addition of cryptand [2.2.2] or THF to toluene increases the degradation rate. The solvation of alkali metal cations with more polar solvents facilitates chemical degradation, due to stabilization of radical anions. The rate of degradation increases with the reactivity of the alkali metal. Poly(methylphenylsilylene) degrades with K faster than with Na, but does not degrade with Li. The application of ultrasound helps to clean the metal (Li) surface by cavitational erosion but does not change the rate of degradation. Poly(di-n-hexylsilylene) degrades only with K, but does not degrade with Na or Li, even if the the metal surface is activated by ultrasound. These results indicate that the reactivity of alkali metals decreases in the order: K > Na > Li. This reactivity order is consistent with the results obtained from the reductive coupling of dichlorosilanes with alkali metals[7]. The effect of the counterion seems to be less important, since degradation, initiated by sodium and lithium naphthalenides, proceeds nearly as fast as with potassium.

Degradation is much faster for poly(methylphenylsilylene) than for poly(di-n-hexylsilylene). This is in accord with a general trend in the stability of the silyl anions discussed previously. Aryl groups on the silicon atom stabilize anionic intermediates. Sodium and lithium cannot start the degradation of poly(di-n-hexylsilylene), even in THF solution and even in the presence of ultrasound.

The mechanism of the degradation is shown below in Scheme 3. The first step, in which a polymeric radical anion is formed by an

electron transfer, may be rate limiting. It is facilitated in polar solvents because of the energy gain by the solvation of alkali metal cations. The intermediate radical anion is cleaved to form a radical and an anion. The fate of that radical is not known. It may react with a solvent; it may take a second electron to form a silyl anion; or it may recombine (although the radical concentration is usually very low). The silyl anions may now start cleaving Si-Si bonds. Because of the entropic effects, the rate of intramolecular reaction is much faster than the rate of the intermolecular process. The intermolecular reaction is accompanied by the loss of three degrees of translational freedom. On the other hand, the intramolecular reaction is accompanied by the formation of a ring which might be strained. The anchimeric assistance (or neighboring group participation) is the highest for five- and six-membered rings, which should have the lowest angular strain. It has been observed that five-membered rings are formed by chemical degradation of poly(methylphenylsilylene) (Fig. 8). The back-biting process for larger or smaller rings is retarded for enthalphic or entropic reasons.
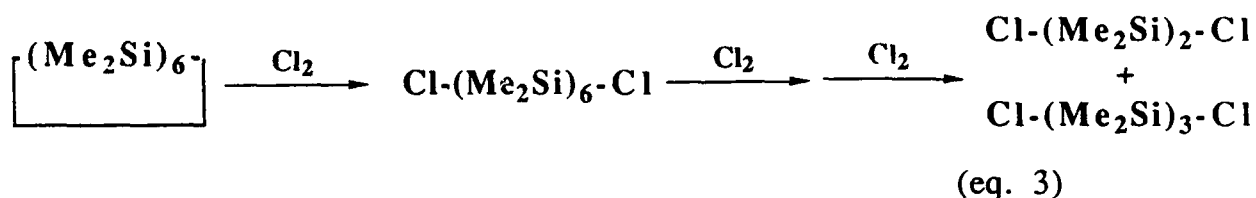
The back-biting process has to be distinguished from the end-biting process which may occur during the synthesis of polysilanes (Scheme 4). Polymerization proceeds by the reaction of silyl anions (which may have some covalent bond character) with dichlorosilane (a monomer) via a chain growth process. At the level of tetra-, penta-, or hexasilane, the anionic center present at one end may react with its chloro-terminated end instead of with a monomer. The end-biting process will lead to the formation of cyclics. Evidence for a different mechanism of end-biting and back-biting processes[5] is

provided by the structure of cyclic oligomers which are formed during the synthesis and during degradation of poly(di-n-hexylsilylene). More than 80% of octa-n-hexylcyclotetrasilane ($\delta = -20.3$ ppm in ^{29}Si NMR) is formed under the reductive coupling process in the mixture of toluene and isooctane. On the other hand, the degradation leads to the formation of deca-n-hexylcyclopentasilanes ($\delta = -34.6$ ppm in ^{29}Si NMR) as shown in Fig. 9.

Present results indicate that the back-biting (or degradation) is not important in toluene without additives. It is also not very important for poly(di-n-hexylsilylene) in THF. However, polymerization of methylphenyldichlorosilane with any alkali metal in THF will result in cyclics rather than in poly(methylphenylsilylene)

B. Cleavage of Si-Si Bonds by Electrophiles

Si-Si bonds are cleaved by electrophiles such as Lewis acids (also halogens) and protonic acid. Cyclic polysilanes form linear α,ω-dihalopolysilanes in the reaction with halogens Dodecamethylcyclohexasilane is cleaved by Cl_2 first to 1,6-dichloropermethylhexasilane which subsequently gives 1,2-dichlorodisilanes and 1,3-trisilanes (eq. 3)[20]. PCl_5 and $SOCl_2$ were also used as chlorinating agents[21]. In a similar way, other halides react to generate α,ω-dibromo- and α,ω-diiodopolysilanes.

$$\boxed{\text{(Me}_2\text{Si)}_6} \xrightarrow{\text{Cl}_2} \text{Cl-(Me}_2\text{Si)}_6\text{-Cl} \xrightarrow{\text{Cl}_2} \xrightarrow{\text{Cl}_2} \begin{array}{c} \text{Cl-(Me}_2\text{Si)}_2\text{-Cl} \\ + \\ \text{Cl-(Me}_2\text{Si)}_3\text{-Cl} \end{array}$$

(eq. 3)

Disilanes and cyclics[22] react with I_2 to provide monoiodosilanes and α,ω-diiodopolysilanes, respectively. Cycles are also cleaved by hydrogen halides such as HCl, HBr or HI. HBr and HI react rapidly, but HCl reacts very slowly[23]. The degradation of high molecular weight polysilanes, such as poly(methylphenylsilylene) or poly(di-n-hexylsilylene), by iodine is shown in Scheme 5. The cleavage of Si-Si bonds in polysilane provides α,ω-difunctional polysilanes. Molecular weights can be controlled by a mole ratio of iodine to silylene unit in a polysilane. For example, a poly(methylphenylsilylene) with a molecular weight of $M_n = 115,000$ was degraded to $M_n = 4,600$ after addition of I_2 to reach [silylene unit]$_o$/[I_2]$_o$ mole ratio of 44 (corresponding to $M_n = 4,900$) The degraded polymers have been reacted with PhMgBr in order to convert unstable Si-I bonds to SiPh groups. SiI bonds hydrolyze and condense in the presence of moisture to a product containing Si-O-Si bonds.

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Captions for Figures

Fig. 1. GPC traces after thermal degradation of poly(methylphenyl-silylene) in a solid state at different temperatures as a function of time.

Fig. 2. UV spectra of solution of the degraded poly(methylphenyl-silylene) in CH_2Cl_2 at 25 °C.

Fig. 3. IR spectrum of poly(methylphenylsilylene) degraded in a solid state at 150 °C in the presence of air.

Fig. 4. GPC traces after thermal degradation of poly(methylphenyl-silylene) in decalin solution at 150 °C (a) and 190 °C (b) as a function of time.

Fig. 5. Plots of M_w versus Ttme in the sonochemical degradation of polysilanes with alkali metals.

Fig. 6. Plots of M_w versus time in the sonochemical degradation of poly(methylphenylsilylene) at various concentrations.

Fig. 7. ^1H NMR spectra of methyl groups in poly(methylphenyl-silylene) (a) and the product degraded by ultrasound (b).
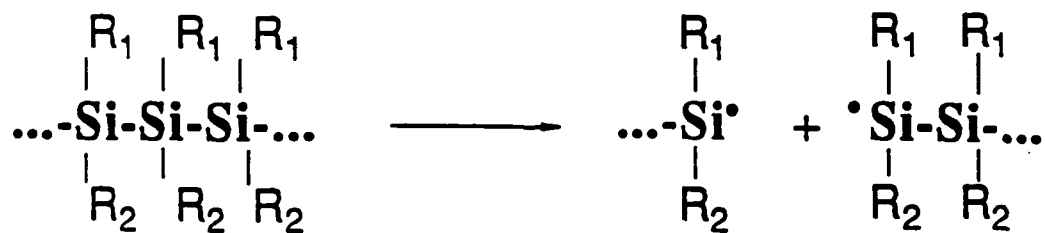
Fig. 8. ^{29}Si NMR spectra of 1,2,3,4,5-pentamethyl-1,2,3,4,5-pentaphenylcyclopentasilanes formed by chemical degradation of poly(methylphenylsilylene) with K.

Fig. 9. ^{29}Si NMR spectra of deca-n-hexylcyclopentasilane formed by chemical degradation of poly(di-n-hexylsilylene) with K.

Scheme 1. Possible Mechanism of Thermal Degradation.

crosslinking
(R_2: aromatic groups)
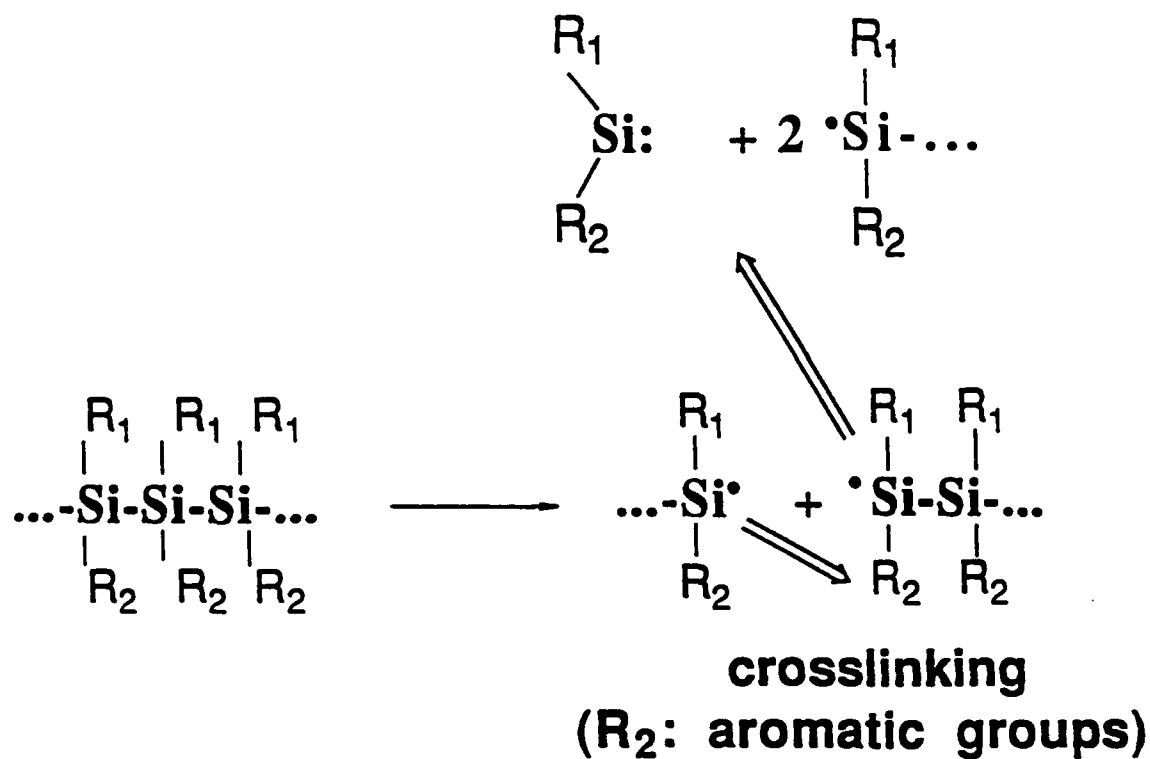
Scheme 2. Homolytic Cleavage of Si-Si Bonds by Ultrasound.

Scheme 3. Chemical Degradation of Polysilanes with Alkali Metals in Three Steps.

...-Si-Si-Si-Si-Si-Si-Si-Si-Si-Si...

$+$ e^-

Mt

1st step

...-Si-Si-Si-Si-Si-Si-Si-Si-Si-Si...

Mt^+

2nd step

...Si-Si-Si-Si-Si-Si$^-$ $+$ $^.$Si-Si-Si-Si...

3rd step

?

...-Si$^-$ $+$

Scheme 4. End-Biting and Back-Biting of Silyl Anions.

$$\underset{\underset{Me \quad Me \quad Me}{|\quad |\quad |}}{\overset{\overset{Ph \quad Ph \quad Ph}{|\quad |\quad |}}{Cl\text{-}Si\text{-}(Si)_m\text{-}Si^-}} Na^+ \xrightarrow{\text{end-biting}} cyclics + NaCl\downarrow$$

$$m = 3 \text{ or } 4; \quad n = m + 1$$

$$\underset{\underset{Me \ Me \quad Me \quad Me}{|\ \ |\quad |\quad |}}{\overset{\overset{Ph Ph \ Ph \quad Ph}{|\ |\quad |\quad |}}{\cdot\text{-}Si\text{-}Si\text{-}(Si)_m\text{-}Si^-}} Na^+ \xrightarrow{\text{back-biting}} \underset{\underset{Me}{|}}{\overset{\overset{Ph}{|}}{....\text{-}Si^-}} Na^+ + cyclics$$
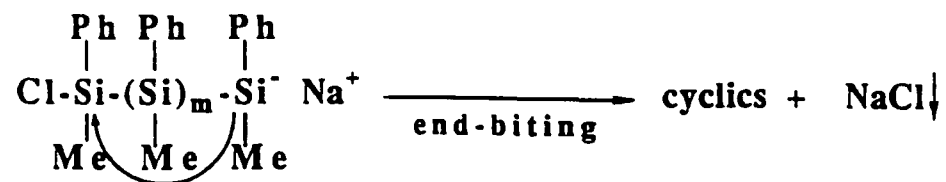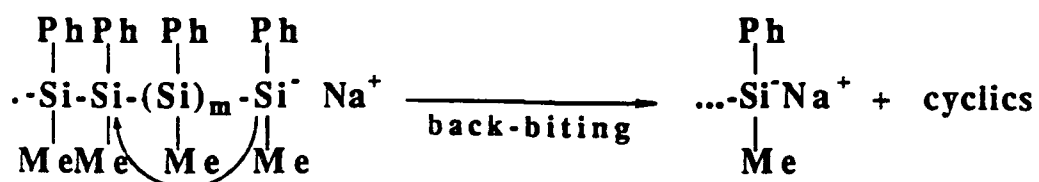
Scheme 5. Chemical Degradation of Polysilanes with Iodine.

$$....\text{-}SiR_2 \vdots SiR_2\text{-}.... + I_2 \xrightarrow{CH_2Cl_2} 2....\text{-}SiR_2\text{-}I$$
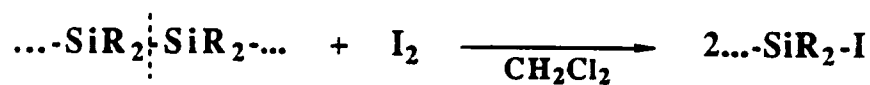
Table1. Results of Sonochemical Degradation of Polysilanes with Na and without Na in a Cleaning Bath.

	poly(phenylmethylsilylene)		poly(dihexylsilylene)
	without Na	with Na	without Na
conc.(% wt) (toluene)	0.8	0.8	0.8
time (min)	$M_w \cdot 10^{-5}$ (M_w/M_n)	$M_w \cdot 10^{-5}$ (M_w/M_n)	$M_w \cdot 10^{-5}$ (M_w/M_n)
0	2.27 (2.68)	2.27 (2.68)	2.98(2.10)
30	1.66 (2.17)	1.28 (1.79)	2.36 (1.90)
60	1.40 (1.96)	1.12 (1.78)	2.11 (1.75)
120	1.37 (1.94)	1.10 (1.78)	1.35 (1.57)
360	1.17 (1.85)	[#]1.02 (1.70)	1.27 (1.49)

\# After the sonication of 24 hrs: $M_w = 8.8 \cdot 10^4$ and $M_w/M_n = 1.17$

Table 2. Summary of Chemical Degradation of Polysilanes with Alkali Metals.

Solvent	Mt	$(PhMeSi)_n$	$(Hex_2Si)_n$
THF	K	v fast	slow
	Na	slow	no
	Li	no	no
	Na^+	v fast	v slow
	Li^+	v fast	v slow
Toluene	K	no	no
	Na	no	no
	#Na	slow	v slow

Li^+ or Na^+: Mt^+ [naphthalenide]$^-$

Addition of cryptand [222] or THF after polymerization

v fast < 10 min; fast < 30 min; slow > 2 hrs;

v slow > 10 hrs; no > 3 days

Fig. 1. GPC Traces of Thermal Degradation of Poly(methylphenyl-silylene) in a Solid State at the Different Temperatures as a Function of Time.
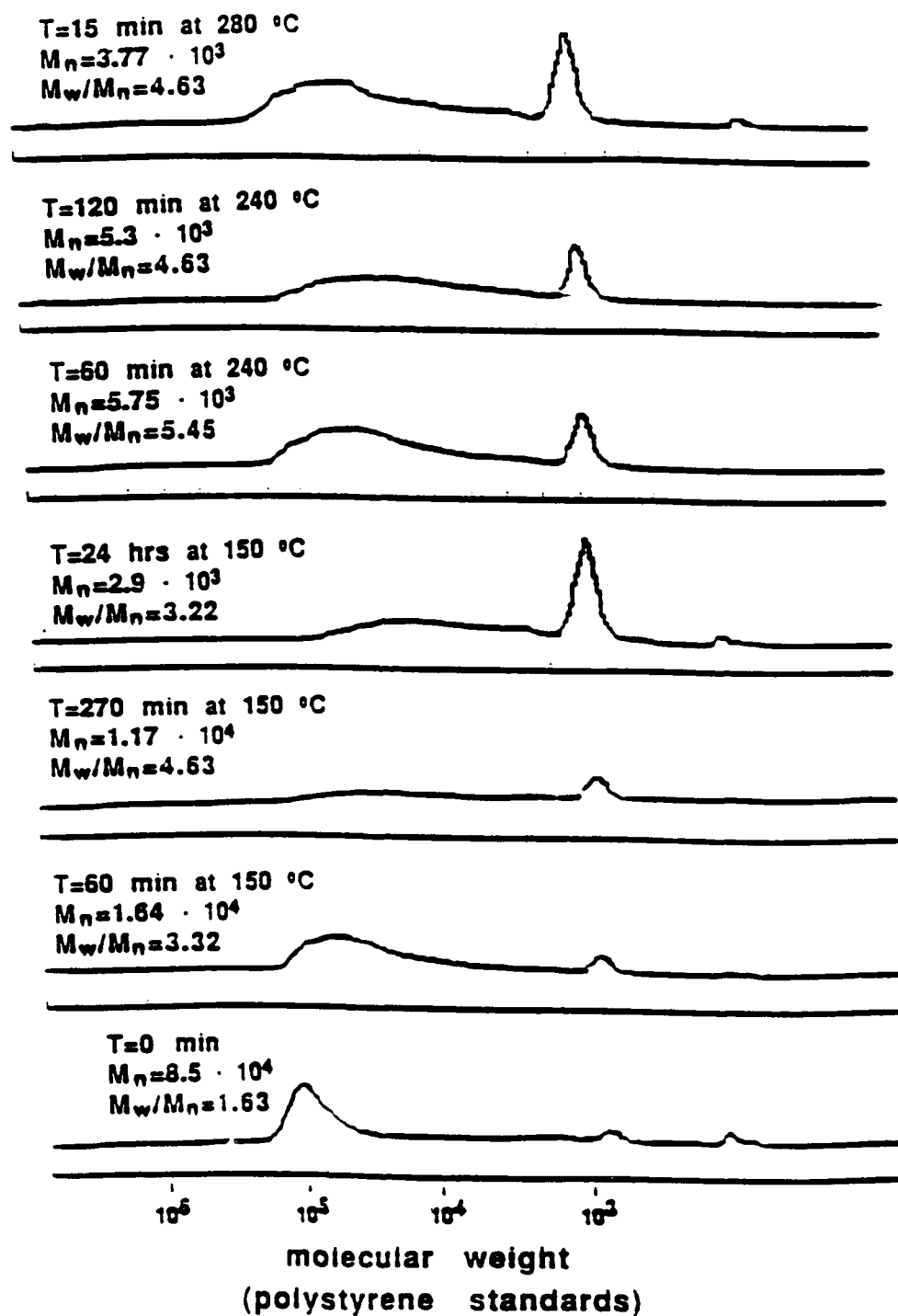

T=15 min at 280 °C
$M_n = 3.77 \cdot 10^3$
$M_w/M_n = 4.63$

T=120 min at 240 °C
$M_n = 5.3 \cdot 10^3$
$M_w/M_n = 4.63$

T=60 min at 240 °C
$M_n = 5.75 \cdot 10^3$
$M_w/M_n = 5.45$

T=24 hrs at 150 °C
$M_n = 2.9 \cdot 10^3$
$M_w/M_n = 3.22$

T=270 min at 150 °C
$M_n = 1.17 \cdot 10^4$
$M_w/M_n = 4.63$

T=60 min at 150 °C
$M_n = 1.64 \cdot 10^4$
$M_w/M_n = 3.32$

T=0 min
$M_n = 8.5 \cdot 10^4$
$M_w/M_n = 1.63$

10^6 10^5 10^4 10^3

molecular weight
(polystyrene standards)

Fig. 2. UV Spectrum of Solution of the Degraded Poly(methylphenylsilane) in CH_2Cl_2 at 25 °C.
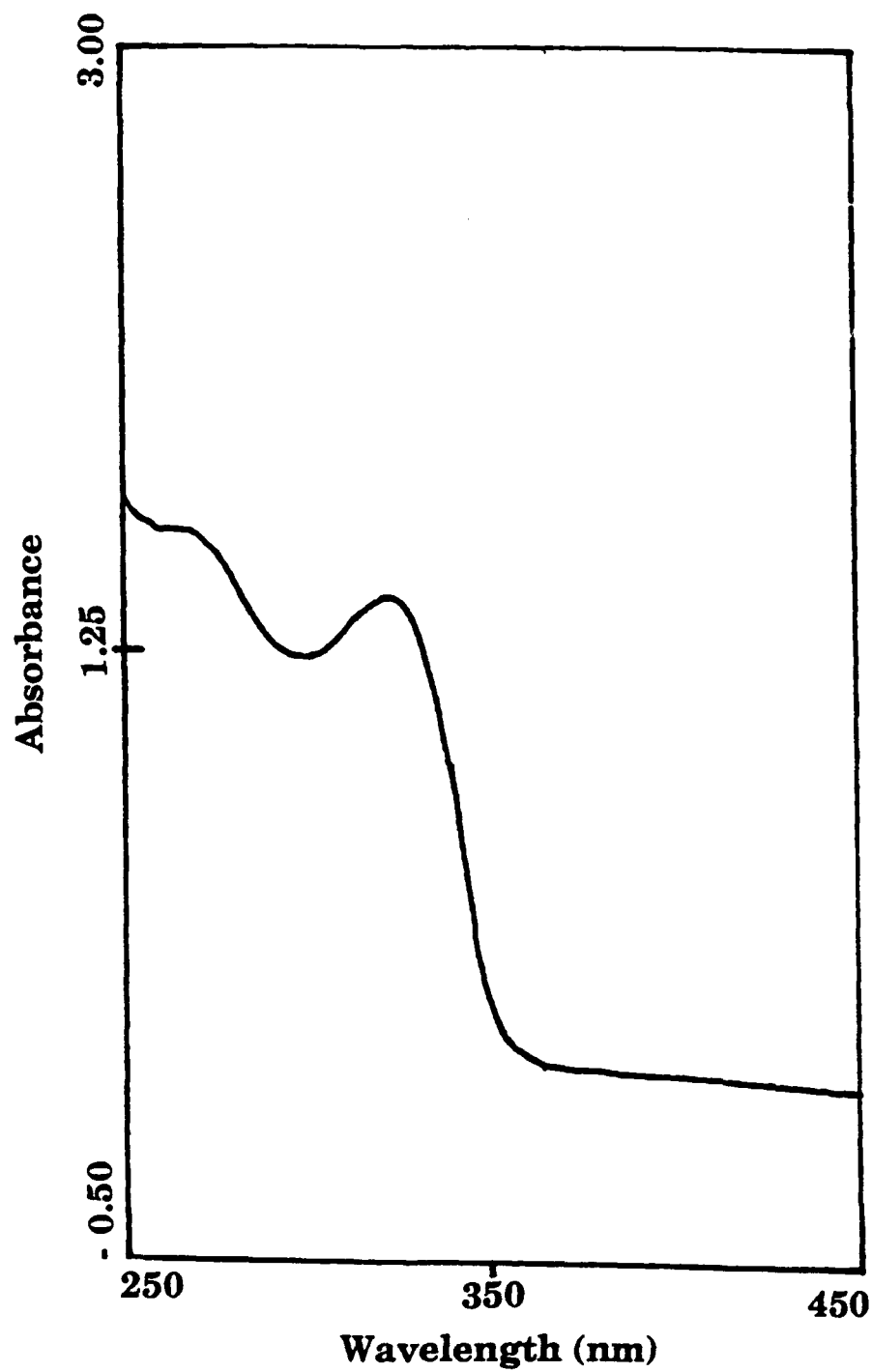
Fig. 3. GPC Traces of Thermal Degradation of in Solution at the Different Temperatures as a Function of Time: (a) 150 °C and (b) 190 °C
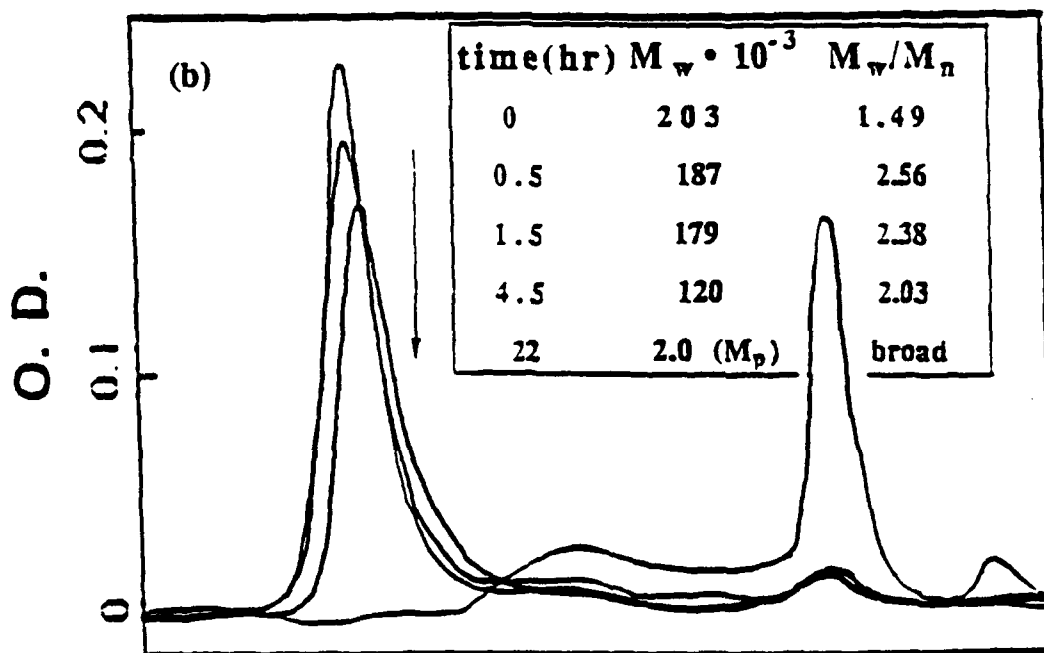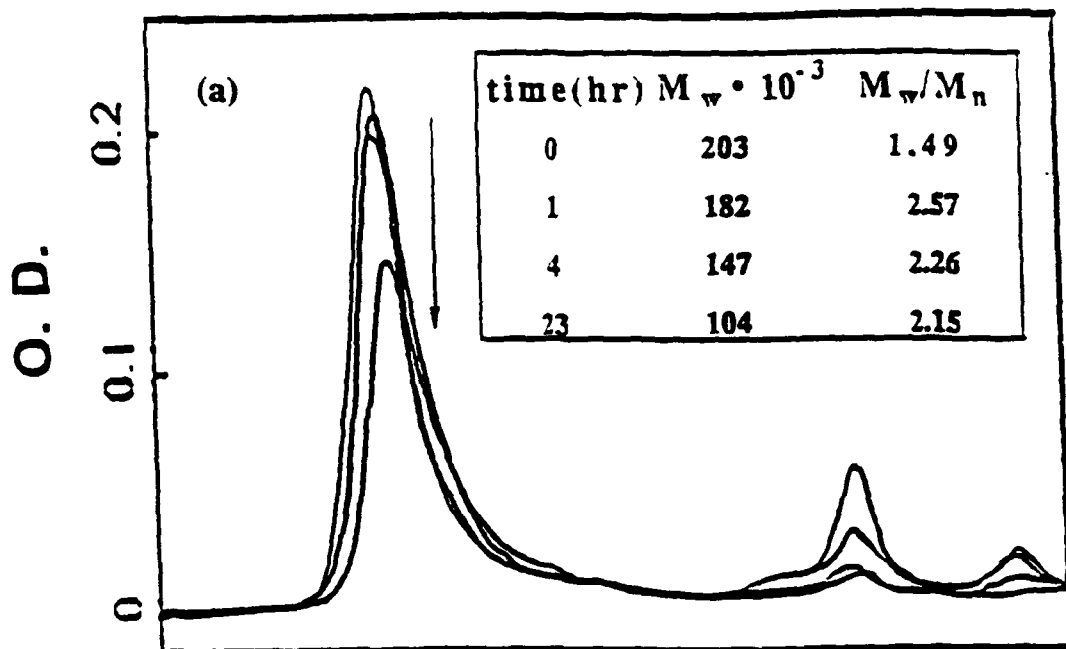

(a)

time(hr)	$M_w \cdot 10^{-3}$	M_w/M_n
0	203	1.49
1	182	2.57
4	147	2.26
23	104	2.15

(b)

time(hr)	$M_w \cdot 10^{-3}$	M_w/M_n
0	203	1.49
0.5	187	2.56
1.5	179	2.38
4.5	120	2.03
22	2.0 (M_p)	broad

Fig. 4. IR Spectrum of the Degraded Poly(methylphenylsilylene) at 150 °C in a Solid State in the Presence of Air.
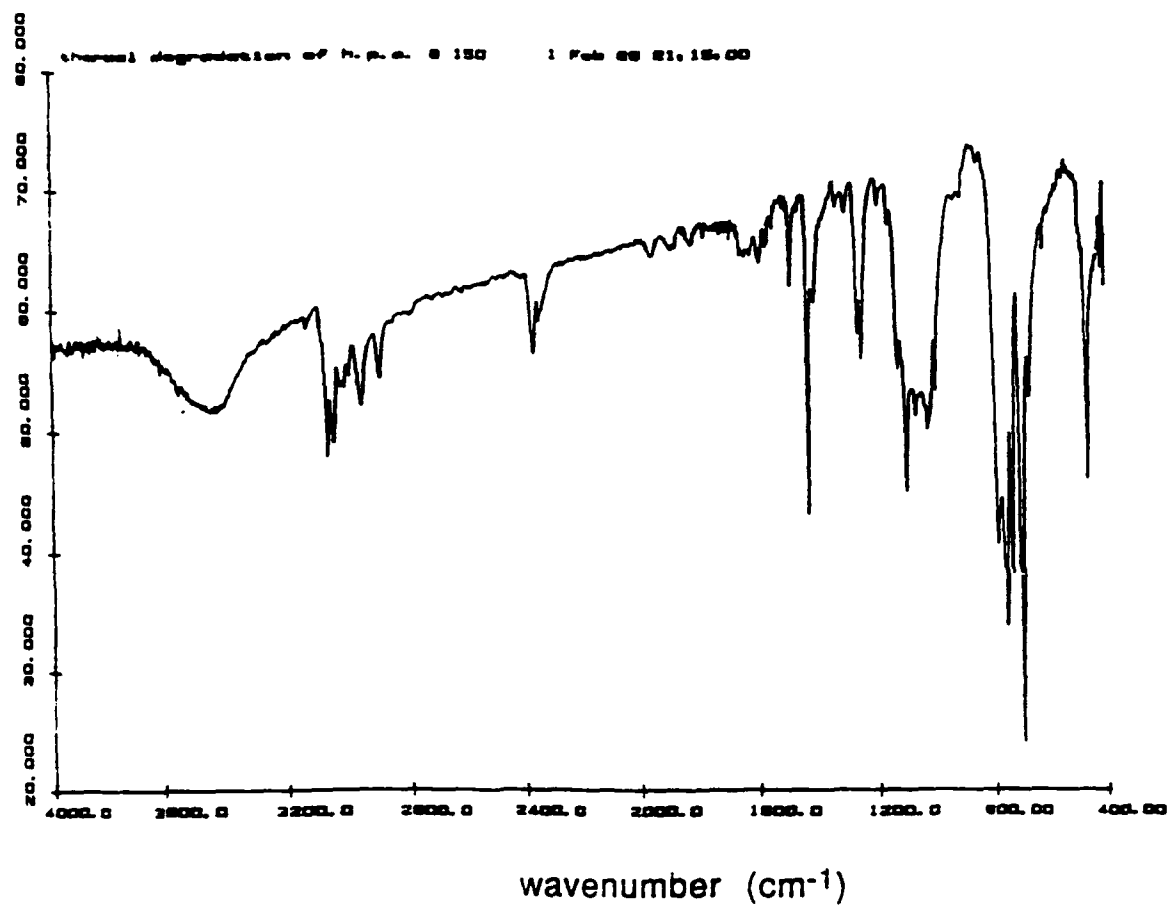

wavenumber (cm⁻¹)

Fig. 5. ^{1}H NMR Spectra of Methyl Groups in Poly(methylphenylsilylene) (a) and the Degraded Product (b) by Ultrasound in CDCl₃.
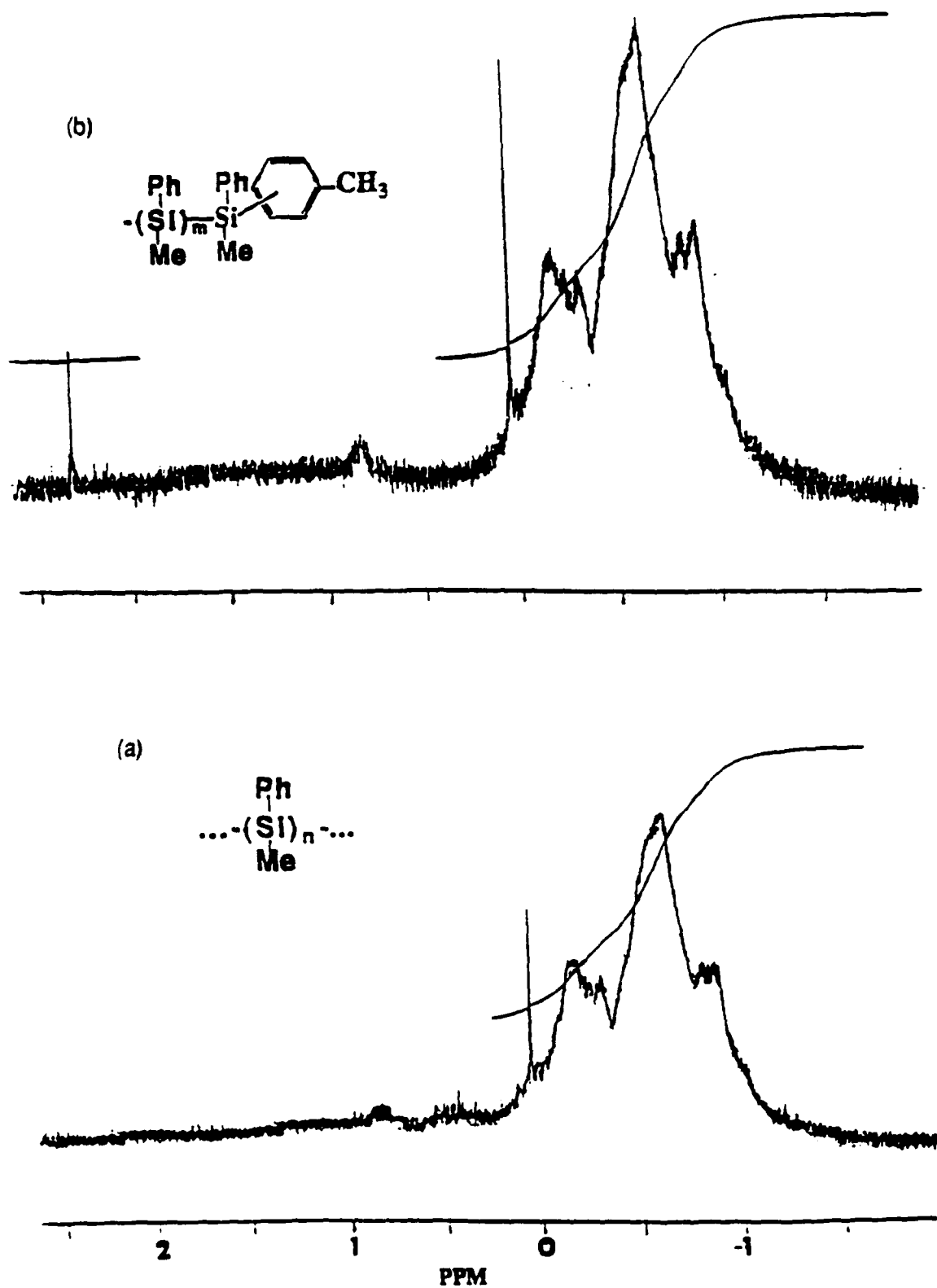

(b)

(a)

Fig. 6. Plots of M_w versus Time in the Sonochemical Degradation of Polysilanes with Alkali Metals.
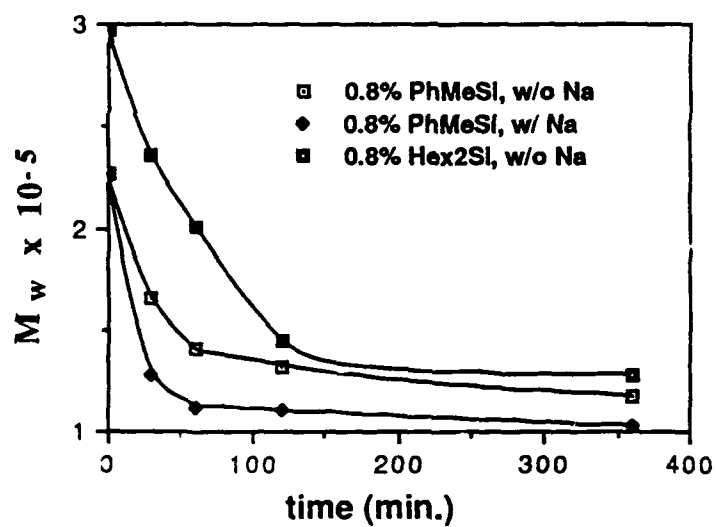
Fig. 7. Plots of M_w versus Time in the Sonochemical Degradation of Polysilanes at Various Concentrations.
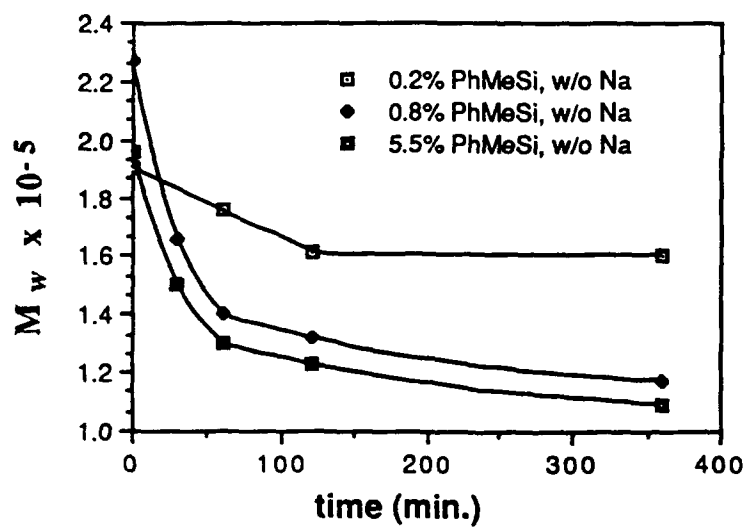
Fig. 8. ^{29}Si NMR Spectra of Pentamethylpentaphenylcyclopentasilane Formed by Chemical Degradation of Poly(methylphenylsilylene) with K in $CDCl_3$.
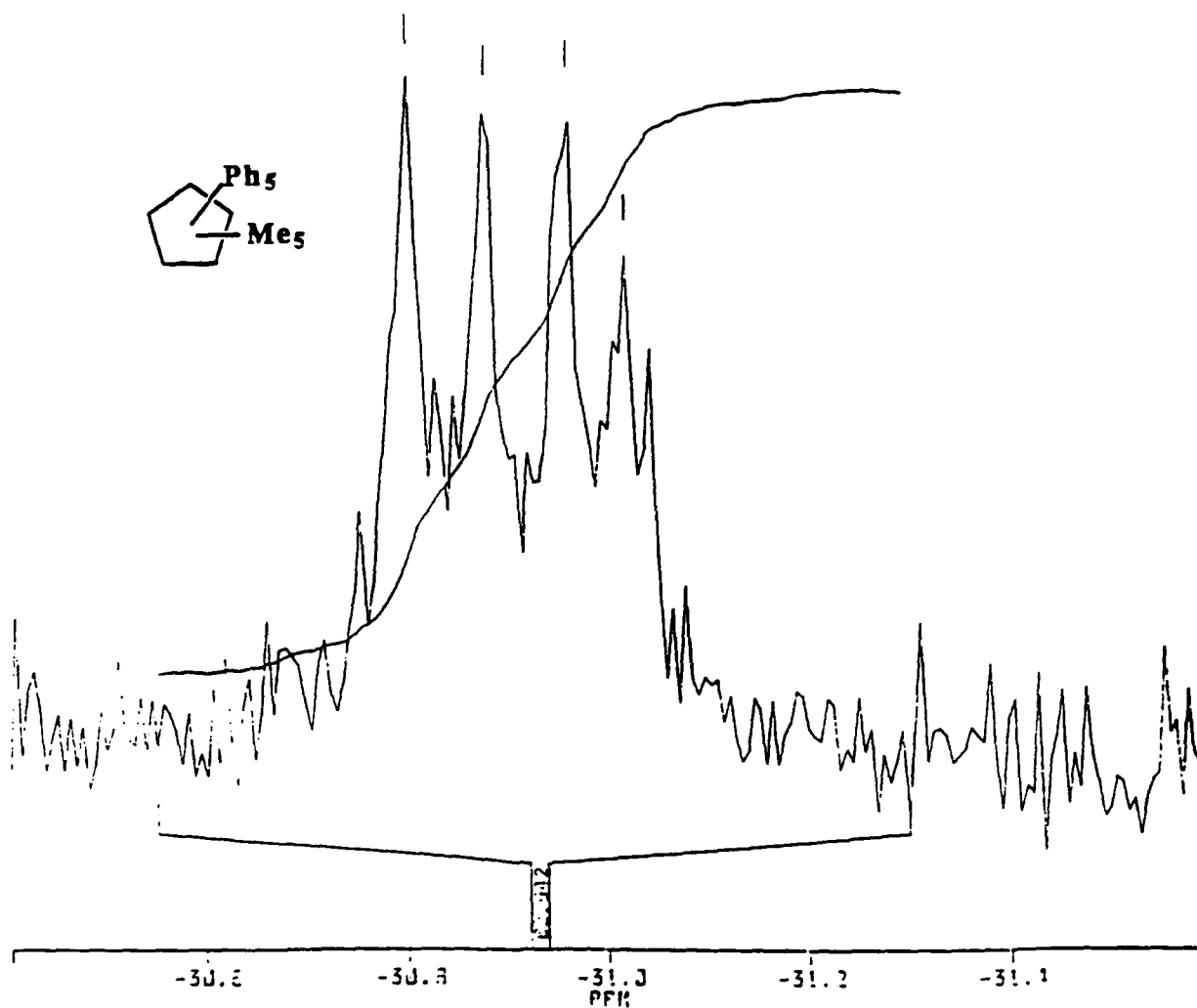
Fig. 9. ^{29}Si NMR Spectra of Decahexylcyclopentasilane Formed by Chemical Degradation of Poly(di-n-hexylsilylene) with K in $CDCl_3$.